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(New) The protective layer according to claim 17, wherein:

the gas-permeable carrier includes a block having a plurality of tubes arranged side by side in a radial alignment relative to one of a straight line and a point.

(21)

(New) The protective layer according to claim 20, wherein:

the tubes have a cross section that tapers toward the one of the straight line and the point.

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(New) The protective layer according to claim 13, wherein:

the gas-permeable carrier includes at least one grid having intersecting grid rods that are provided with the oxidizing agent.

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(New) The protective layer according to claim 22, wherein:

the gas-permeable carrier includes a block having a plurality of grids stacked one above the other.

24)

(New) A CO<sub>2</sub> sensor, comprising:

a protective layer including:

a gas-permeable carrier made of a material that is resistant to sulfuric acid media including SO<sub>2</sub> and SO<sub>3</sub>, and

a surface that can be exposed to a gas and is provided with an oxidizing agent having an oxidation potential that is sufficient to oxidize SO<sub>2</sub>, the protective layer separating the CO<sub>2</sub> sensor from a room to be monitored for a CO<sub>2</sub> content.

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(New) The CO<sub>2</sub> sensor according to claim 24, wherein:

the CO<sub>2</sub> sensor is for a smoke detector.

#### Remarks

This Preliminary Amendment cancels original claims 1 to 12 without prejudice, in the underlying PCT Application No. PCT/DE00/00406. The Preliminary Amendment also adds

new claims 13-25. The new claims conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. § 1.121(b)(3)(iii) and § 1.125(b)(2), a Marked Up Version Of The Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) are respectfully requested.

The underlying PCT Application No. PCT/DE00/00406 includes an International Search Report, dated July 14, 2000, and an International Preliminary Examination Report, dated March 28, 2001, copies of which are submitted herewith.

Applicants assert that the subject matter of the present application is new, nonobvious, and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully Submitted,

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Dated: 8/13/01

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[10191/1977]

#### PROTECTIVE LAYER

## Field Of The Invention [Background Information]

The present invention relates to a protective layer which is relatively permeable for CO<sub>2</sub> and is relatively impermeable for SO<sub>2</sub>.

## **Background Information**

Such a protective layer is used, for example, to protect a CO<sub>2</sub>-sensitive polymer layer of a smoke detector from damage or contamination due to SO<sub>2</sub>. Such a CO<sub>2</sub>-sensitive polymer layer is used as a gas sensor in a smoke detector to detect a CO<sub>2</sub> content in a room where the smoke detector is installed. The CO<sub>2</sub>-sensitive polymer layer preferably has a membrane composed of a polymer matrix (e.g., polydimethylsiloxane), an auxiliary base (tetraalkylammonium hydroxide) and a pH-sensitive dye (e.g., thymol blue or other derivatives). When this CO<sub>2</sub>-sensitive membrane is exposed to CO<sub>2</sub>, it leads to reversible reactions, preferably detectable by an optical [means] element, in particular also by electrical or mass-sensitive [means] elements, thus permitting an inference regarding the CO<sub>2</sub> content in the room monitored.

However, when this CO<sub>2</sub>-sensitive membrane comes in contact with SO<sub>2</sub>, it leads to irreversible reactions in the sensor material and thus to destruction of the CO<sub>2</sub>-sensitive feature of the sensor. Since this reaction of the sensor membrane to SO<sub>2</sub> is irreversible, SO<sub>2</sub> reaction products accumulate on the membrane, so that even a low SO<sub>2</sub> concentration will damage the sensor membrane over a period of time and decreases its CO<sub>2</sub> sensitivity, so that a smoke detector equipped with such a CO<sub>2</sub>-sensitive membrane sensor will ultimately become useless.

Known protective layers are designed as compressed powder pellets or granules which are

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relatively impermeable for SO<sub>2</sub> but relatively permeable for CO<sub>2</sub>. Likewise, there are known molecular filters which utilize differences in the molecular structure of the CO<sub>2</sub> molecules and are thus relatively impermeable for SO<sub>2</sub> molecules and relatively permeable for CO<sub>2</sub> molecules. However, one disadvantage when such a protective layer is used to protect a CO<sub>2</sub> sensor is that the CO<sub>2</sub> molecules must first penetrate through this protective layer to reach the CO<sub>2</sub> sensor. Accordingly, the period of time needed for the CO<sub>2</sub> molecules to reach the CO<sub>2</sub> sensor may be greatly prolonged. This increase in time has an especially serious effect when the CO<sub>2</sub> molecules are in movement merely due to their temperature-related kinetic energy (Brownian motion) in the absence of a directional flow, which is usually the case in propagation of smoke in the event of a fire. When such a protective layer is then used in a smoke alarm, the response time of the smoke alarm is increased due to the period of time required for the gas molecules to penetrate through the protective layer; in other words, the period of time until the CO<sub>2</sub> sensor detects an elevated CO<sub>2</sub> concentration is longer.

## [Advantages of the] Summary Of The Invention

The protective layer according to the present invention [having the features of Claim 1], however, has the advantage that the CO<sub>2</sub> molecules need only a relatively short period of time to penetrate through the protective layer. When using the protective layer according to the present invention in a smoke alarm, this yields the advantage that the lengthening of the response time of the smoke alarm due to the protective layer is reduced.

The present invention is based on the finding that the oxidation product of  $SO_2$ , namely  $SO_3$ , is a strongly oxidizing and hygroscopic acid anhydride which reacts further immediately to form a sulfate ( $SO_4^{2-}$ ). However the resulting sulfates may be deposited on the carrier material, so that sulfates are adsorbed in the protective layer.

SO<sub>2</sub> molecules thus accumulate on the carrier and are stored there, while CO<sub>2</sub> molecules can penetrate through the protective layer without reacting. Theoretically, a single contact of an SO<sub>2</sub> molecule with the carrier surface provided with the oxidizing agent is sufficient to trigger the above-mentioned reaction, so complicated structures (such as those in a compressed powder pellet, for example) need not be formed in the protective layer to guarantee this one

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contact with a probability bordering on certainty. Accordingly, CO<sub>2</sub> molecules need not penetrate through any complicated protective layer structure, so that CO<sub>2</sub> molecules can penetrate through the protective layer according to the present invention in a relatively unhindered and undelayed manner.

According to a preferred embodiment, the carrier may have at least one tube whose inside wall is provided with the oxidizing agent. In this embodiment, the SO<sub>2</sub> molecules and the CO<sub>2</sub> molecules [must] penetrate through this tube axially, in which case there is a probability according to the laws of probability for the molecules striking the inside wall of the tube coated with the oxidizing agent. Due to this contact, an SO<sub>2</sub> molecule may become adsorbed on the carrier while a CO<sub>2</sub> molecule will rebound away from it without reacting and will continue on its way. The value for this adsorption probability can be determined as a function of a mean length of free path of the molecules by using a ratio of the cross section of the tube to the length of the tube.

[Other important features and advantages of the protective layer according to the present invention are derived from the subordinate claims, the drawings and the respective description of the figures on the basis of the drawings.] <u>Brief Description Of The Drawings</u>

[Embodiments of the protective layer according to the present invention are shown in the drawings and are illustrated in greater detail below. The drawings show schematically:]

Figure 1 shows a longitudinal section through a first embodiment of the protective layer according to the present invention[,]

Figure 2 shows a perspective view of a second embodiment of the protective layer according to the present invention[,]

Figure 3 shows a side view of a third embodiment of the present invention[, and]

Figure [4] 4a shows a side view [(Figure 4a) and a top view (Figure 4b)] of a fourth embodiment of the protective layer according to the present invention.

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Figure 4b shows a top view of a fourth embodiment according to the present invention.

# **Detailed Description** [of Embodiments]

According to Figure 1, a smoke detector 3 is mounted on a wall 2 in a room 1, in particular on a room ceiling; in the event smoke develops in room 1, this smoke detector should deliver a warning signal accordingly. For this purpose, smoke detector 3 has a CO<sub>2</sub>-sensitive sensor 4 equipped with a CO<sub>2</sub>-sensitive membrane 5. In addition, smoke detector 3 has a carrier 10, which is designed here as a cylindrical tube 6, in particular a round cylindrical tube. In this embodiment, this tube 6 is part of a protective layer 7 according to the present invention which is marked by figure bracket 7. CO<sub>2</sub> sensor 4 here is separated from room 1 by this protective layer 7, i.e., by tube 6.

Tube 6 is mounted in an airtight mount on smoke detector 3 on one axial end, so that tube 6 encloses CO<sub>2</sub> sensor 4. The axial end of tube 6 opposite CO<sub>2</sub> sensor 4 is open and exposed to a gas present in room 1. An inside wall 8 of tube 6 is provided with a coating 9 of a nonvolatile oxidating agent. For example, potassium permanganate may be used as the oxidizing agent. Tube 6 may be made of aluminum oxide, for example.

The protective layer according to the present invention functions as follows:

As soon as an SO<sub>2</sub> molecule strikes inside wall 8 of tube 6 (the path of motion of such an SO<sub>2</sub> molecule is represented by an interrupted line), the SO<sub>2</sub> molecule is oxidized to an SO<sub>3</sub> molecule by the oxidizing agent, forming manganese dioxide (MnO<sub>2</sub>). The acid anhydride SO<sub>3</sub> immediately reacts further to (SO<sub>4</sub><sup>2-</sup>) and combines with released potassium compounds to form K<sub>2</sub>SO<sub>4</sub>. The solids formed by these reactions, namely MnO<sub>2</sub> and K<sub>2</sub>SO<sub>4</sub>, are deposited on inside wall 8 of tube 6, so that to this extent the SO<sub>2</sub> molecules are adsorbed by carrier 10 of layer 7 or by tube 6. Tube 6 is preferably made of a corrosion-resistant material that is resistant to sulfuric acid media, so that neither SO<sub>2</sub> nor SO<sub>3</sub> molecules nor (SO<sub>4</sub><sup>2-</sup>) can damage tube 6.

In contrast with an SO<sub>2</sub> molecule, a CO<sub>2</sub> molecule (its path of motion represented by a solid

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line) is not adsorbed on inside wall 8 of tube 6, but instead is deflected, so that the CO<sub>2</sub> molecule can strike membrane 5 of CO<sub>2</sub> sensor 4 without any great delay. As soon as a sufficient quantity of CO<sub>2</sub> molecules striking membrane 5 has triggered the proper response, smoke alarm 3 delivers the warning signal.

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According to Figure 2, carrier 10 of protective layer 7 according to the present invention may also be designed as a block which may be composed of a plurality of axially parallel cylindrical tubes 6 arranged side by side. In this embodiment, tubes 6 have a rectangular cross section, in particular a square cross section. Here again, inside walls 8 are provided with oxidizing agent coating 9.

Such block-like carriers 10 can be produced especially easily from monolithic catalysts, which then need only be provided with oxidizing agent coating 9.

According to Figure 3, carrier 10 of protective layer 7 may also be designed as a block, individual tubes 6 aligned radially with respect to a straight line perpendicular to the plane of the drawing or a point 11. In the specific embodiment illustrated in Figure 3, tubes 6 are not cylindrical in shape but instead they have a cross section tapering in the direction of the point or line 11. This embodiment allows molecules to penetrate into tubes 6 from a large solid angle range, so that CO<sub>2</sub> molecules can reach CO<sub>2</sub> sensor 4 from practically all directions.

According to Figures 4a and 4b, carrier 10 of protective layer 7 is again formed from a block, which here is composed of multiple grids 12 stacked one above the other, each being formed by a plurality of intersecting grid rods 13. Individual grids 12 need not be aligned with one another and stacked as in Figures 4a and 4b, and instead individual grids 12 may also be arranged with an offset. Oxide coating 9 here is applied to the surface of grid rods 13. The probability of adsorption is determined by the number of grids 12 stacked together and by their mesh; in other words, this is the probability that an SO<sub>2</sub> molecule penetrating into protective layer 7 will strike the surface of one of grid rods 13 and will react with the oxidizing agent there, thus being adsorbed in protective layer 7.